

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements relating to the Extraction of Nickel, Cobalt and Iron from Laterite Ore

We, THE INTERNATIONAL NICKEL COMPANY OF CANADA LIMITED, a Canadian Company, of Copper Cliff, Province of Ontario, Canada, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

- Lateritic nickel ores are the nickel-enriched residual products of laterisation of nickel-bearing protore. The laterisation process involves the leaching of magnesia and silica from the ore by atmospheric water in a warm and humid climate. The present invention is concerned with the ores forming the final products of this process, which contain less than 10% magnesia. In most cases these ores contain more than 35% iron, and generally speaking about 1 to 2% nickel and about one-tenth as much cobalt, all percentages being by weight. They are quite widely distributed, and are found in such countries as Brazil, Cuba, Dominican Republic, New Caledonia, and the Philippine Islands.
- Numerous processes have been proposed for the extraction of nickel and cobalt from lateritic nickel ores, including direct acid leaching of the raw ore, smelting to ferro-nickel, sulphating, chloridising, and, after preliminary reduction, leaching with acid or ammoniacal solutions or extraction with carbon monoxide. In particular, in our application No. 5911/57 (Serial No. 855,544) we have described and claimed a process for the extraction of nickel and iron as carbonyls from a lateritic nickel-bearing ore by subjecting the ore to reduction and thereafter to treatment with carbon monoxide at atmospheric pressure and at a temperature between 25°C and 75°C, in which the reduction is carried out within the temperature range 500 to 850°C and in a selectively reducing atmosphere containing carbon monoxide and carbon dioxide in a ratio of not more than 3 : 2

and not less than 1 : 3 by volume, the temperature and composition of the reducing gas being so regulated that the subsequent treatment with carbon monoxide yields a mixture of volatilised nickel and iron carbonyls in which the ratio of iron to nickel is not more than 2 : 1 and not less than 1 : 7 by weight. The carbon monoxide and carbon dioxide in the reducing atmosphere may be partly or wholly replaced by hydrogen and water vapour in an equivalent ratio. Any cobalt present in the ore remains in the solid residue from the treatment with carbon monoxide, from which it may be extracted, together with any residual nickel, by leaching with an ammoniacal solution of ammonium carbonate. This process suffers from the disadvantage that an important proportion of the cobalt is lost through co-precipitation with iron and, as a result, overall cobalt extractions seldom exceed 80%. The other processes proposed suffer from unduly high cost or from unduly low nickel and cobalt extraction or from complexity of operations in the recovery of nickel, cobalt and iron of desired purity.

The present invention provides a process of extracting the nickel, cobalt, and part of the iron from a lateritic ore of the iron oxide type by a novel combination of carbonyl extraction and chloridisation and leaching steps.

The basis of the invention is the discovery that the selective gaseous reduction of the nickel, cobalt, and part of the iron at elevated temperatures followed by extraction of most of the nickel and part of the iron as carbonyls leaves the residue in such a state that the cobalt and the remaining part of the nickel can readily be converted into chlorides by treatment with dry chlorine gas at relatively low temperatures and extracted by leaching with water so as to give a high overall extraction of nickel and cobalt from the ore.

- According to the invention, a lateritic nickel ore containing less than 10% magnesia by weight is reduced by heating it to an elevated temperature in a selectively reducing atmosphere so as to convert substantially all of the cobalt and the nickel contents of the ore and a minor proportion of the iron content of the ore to metal, the reduced ore is cooled in a non-oxidising atmosphere and treated with carbon monoxide so as to volatilise most of the nickel and a small proportion of the iron as carbonyls, the residue is treated with dry chlorine to convert the remaining nickel and the cobalt to the water-soluble state, and the chloridised product is heated in an oxidising gas containing free oxygen to decompose any iron chlorides formed and finally leached with water to remove substantially all the remaining nickel and cobalt.
- The pregnant solution obtained from the leaching operation may be treated in any desired manner. The nickel and cobalt may, for example, be precipitated as sulphides by treating the solution with sodium sulphide or hydrogen sulphide and the precipitated sulphides, after filtration, drying and melting, may be cast into anodes and electrolysed to yield pure electro-nickel, electro-cobalt and sulphur as disclosed in the Renzoni et al U.S. Patent No. 2,839,461.
- To facilitate the formation of nickel carbonyl when the reduced ore is treated with carbon monoxide, a small amount of a sulphur-containing substance, for example, sulphur, pyrite or hydrogen sulphide may be added to the ore at some stage before the carbon monoxide treatment.
- To extract the highest proportion of both nickel and cobalt from the ore, the conditions in both the selective reduction and chloridising steps must be carefully controlled. The temperature in the reduction operation is preferably between 500 and 650°C, although temperatures up to 815°C may be used when the iron content of the ore is relatively low, e.g. less than 35% iron by weight. Since formation of the carbonyls and chlorides are relatively low temperature gas-solid reactions, it is essential to have the metals in an active state, with high surface area, to obtain high and rapid metal extractions. If the selective reduction is carried out above 815°C, a nickel-iron alloy is formed which is relatively inactive and leads to a decrease in both rate and extent of nickel extraction. At temperatures below 500°C the rate and extent of oxide reduction are low, although highly active metal may be obtained in time.
- The selectively reducing atmosphere is preferably one containing carbon monoxide and carbon dioxide in a ratio of not more than 3 : 2 and not less than 1 : 3 by volume, and the reduction is continued until the reduced ore is substantially in equilibrium with the reducing atmosphere. It will be appreciated

that the composition of the atmosphere will generally change during the reduction as it reacts with the ore, and the ratios of carbon monoxide to carbon dioxide refer to the gas mixture with which the reduced ore is substantially in equilibrium at the end of the reaction. The use of a more strongly reducing atmosphere yields a relatively inactive ferro-nickel rich in iron with resulting detriment to nickel and cobalt extraction and consequent lower recoveries of these metals. On the other hand, the use of an atmosphere having a lower ratio of carbon monoxide to carbon dioxide than 1 : 3 results in a decrease in rate and extent of reduction of nickel and cobalt to metal.

The carbon monoxide and carbon dioxide in the reducing gases may be partly or wholly replaced by hydrogen and water vapour in an equivalent ratio, which may be obtained from the equation:



where K is the equilibrium constant for the reversible reaction:

$CO + H_2O \rightleftharpoons CO_2 + H_2$

and depends on the temperature. The values of K at different temperatures are given in the literature, approximate values in the temperature range 500-850°C being:

| Temperature (°C) | K. | 95 |
|---------------------|------|-----|
| 527 | 0.25 | |
| 627 | 0.45 | |
| 727 | 0.72 | |
| 827 | 1.0 | 100 |

Within the preferred ranges of temperature and composition of the reducing atmosphere set forth above the reduction should be so controlled that the iron reduced to the metallic state is not less than 1% but less than 15% of the iron content of the ore. If this is done, it is possible subsequently to volatilise up to 90% of the nickel content of the ore as nickel carbonyl. If more than 15% of the iron is reduced to the metallic state, volatilisation of nickel as carbonyl from the iron-rich alloy becomes difficult and the proportion of metallic nickel obtainable by this means is decreased and the amount of iron converted to chloride on subsequent treatment with chlorine is increased. On the other hand the reduction of substantially all the nickel and cobalt to metal cannot be achieved without the simultaneous reduction of at least 1% of the iron.

When the reduction is complete, the selectively reduced material is cooled in an oxygen-free atmosphere, such as partially spent reduction gas, and then treated with carbon monoxide. This treatment is preferably carried out at a temperature not less than 38°C and not more than 93°C and at atmospheric pressure, and results, if the reduction has been carried out in the pre-

ferred manner, in the volatilisation of a large proportion of the nickel in the ore as nickel carbonyl together with such an amount of iron as iron carbonyl that the ratio of iron to nickel in the volatilised carbonyls is not less than 1 : 7 and not more than 2 : 1. The treatment with carbon monoxide can if desired be carried out under elevated pressure in order to increase the rate of reaction, but this is usually not economically advantageous due to the accompanying increase in cost of equipment required to safely handle the large tonnages of material, only a small fraction of which is to be volatilised.

15 The mixed carbonyls of nickel and iron may be separated in any desired manner, e.g., by liquefaction and fractionation, and the separated carbonyls then decomposed to yield high purity metallic nickel and high purity metallic iron.

20 The residue from the carbonyl extraction operation, i.e., the solids discharged from the volatiliser, is treated with dry chlorine gas to convert the cobalt and the remaining nickel to chlorides. This treatment is preferably carried out at about atmospheric pressure and at a temperature of not less than 38°C and not more than 93°C, i.e. at substantially the same temperature as the carbon monoxide treatment. The amount of chlorine required is about 0.25 to 2.5% by weight of the solids, and the reaction is usually rapidly completed in less than 30 minutes. Owing to the extremely active state of the residual nickel and the cobalt after the carbonyl extraction operation substantially complete chlorination of the cobalt and nickel is achieved under these conditions. A small amount of iron may simultaneously be converted to chloride. If the treatment with dry chlorine gas is carried out at a substantially higher temperature than 93°C, the iron oxides, wustite and magnetite, will undesirably consume chlorine. On the other hand operating at substantially lower temperature than 38°C slows the reaction rate and may require refrigeration with its attendant obvious disadvantages.

25 In order to decompose any iron chlorides formed, air is next substituted for chlorine and the material is heated in air at a temperature between 93 and 260°C at atmospheric pressure for up to 60 minutes. The addition of air must be carefully controlled because some of the iron oxides are pyrophoric and tend to cause high localised temperatures resulting in decreased subsequent nickel and cobalt extractions. It is therefore preferred initially to admit air containing less than normal oxygen content, e.g. air that has been diluted with inert gas, and gradually increase to normal oxygen content or even higher, e.g. by oxygen addition.

30 The chloridised and heat-treated material is then leached with water to extract its nickel and cobalt content.

after carbonylation

not a problem

By means of the process according to the invention up to 99% of the nickel content of the ore may be extracted as carbonyl and chloride, up to 95% of its cobalt content as chloride and a significant percentage of its iron content as carbonyl. The residue is rich in iron and may contain as little as 0.02% nickel and 0.01% cobalt and be suitable for use in steel production.

As compared with the chloridising and leaching of the reduced ore without previous treatment with carbon monoxide, the extraction of the major part of the nickel content of the ore and part of the iron as carbonyls is found to enable a greater proportion of the nickel and cobalt present to be extracted. The reasons for this improvement are thought to be the following:

1. Cobalt and residual nickel become more reactive to chlorine because in the course of the extraction of nickel and iron as carbonyls the porosity or permeability of the ore particles, i.e. the surface area exposed to gas-solid contact, is increased.

2. The pregnant solution obtained by chloridisation and water leaching of the carbonyl-extracted ore contains a much lower nickel to cobalt ratio than that of the original ore. This provides a distinct advantage in subsequent separation to obtain pure cobalt.

3. Since only a minor proportion of the nickel content of the ore is involved in the leaching operation, removal of nickel and cobalt from pregnant solution by chemical precipitation as sulphides, e.g., by sodium sulphide or hydrogen sulphide, is economically practicable. Furthermore, for the same reason, expensive chlorine regeneration is not necessary.

4. Volatilisation of a major part of the metallic iron as carbonyl results in a decrease of chlorine consumption and ultimately enhances recovery of nickel and cobalt from the aqueous leach solution.

Some examples of the process are given below.

Example I

A lateritic nickel ore with less than 10% MgO, containing 1.07% nickel, 0.14% cobalt and 50% iron was ground so that 6% was retained on a sieve having 200 meshes to the linear inch, mixed with 0.05% pyrite and selectively reduced at a temperature of 510°C for 2 hours in an atmosphere containing carbon monoxide, carbon dioxide, hydrogen and water vapour and having a ratio of carbon monoxide to carbon dioxide of 1 to 2.3 at the above temperature. The selectively reduced ore was cooled to 50°C in a non-oxidising atmosphere and treated in a carbonyl volatiliser at atmospheric pressure with gas containing 92% carbon monoxide. This operation rapidly extracted 90% of the nickel content of the ore without cobalt volatilisation together with 1.2% of the iron content

of the ore as mixed carbonyls having an iron to nickel ratio of 1 : 1.5. The solids from the volatiliser were treated with dry chlorine gas at the rate of 20 pounds of chlorine per ton of solids, at 50°C for 10 minutes, then air was substituted for chlorine and the temperature of the charge was raised to 150°C for 30 minutes. The chloridised material was then leached in water at 24°C, yielding an overall extraction of 93% of the nickel content of the ore, 93% of its cobalt content and 2% of its iron content.

Example II

Lateritic nickel ore of the same composition and grind as used in Example I was similarly treated except that selective reduction was carried out at 650°C using a gaseous mixture having a ratio of CO : CO₂ of 1 : 1.5. Treatment of the reduced and cooled product with carbon monoxide, as in Example I, extracted 76% of the nickel together with 1.7% of the iron content of the ore, while the chlorine treatment and water leaching gave an overall extraction of 99% of the nickel, 95% of the cobalt and 2% of the iron content of the ore.

Example III

Lateritic nickel ore of the same composition and grind as used in Examples I and II was similarly treated except that selective reduction was carried out at 700°C using a gaseous mixture having a ratio of CO : CO₂ of 1 : 1.3. Treatment of the reduced and cooled product with carbon monoxide, as in Examples I and II, extracted 60% of the nickel together with 2% of the iron content of the ore, while the chlorine treatment and water leaching gave an overall extraction of 99% of the nickel, 95% of the cobalt and 2.3% of the iron content of the ore.

WHAT WE CLAIM IS:—

1. A process of extracting nickel, cobalt and iron from a lateritic nickel ore containing less than 10% magnesia which comprises reducing the ore by heating it to an elevated temperature in a selectively reducing atmosphere so as to convert substantially all of the cobalt and the nickel content of the ore and a minor proportion of the iron content of the ore to metal, cooling the reduced ore in a non-oxidising atmosphere, treating it with carbon monoxide so as to volatilise most of

the nickel and a small proportion of the iron as carbonyls, treating the residue with dry chlorine gas to convert the remaining nickel and the cobalt to the water-soluble state, heating the chloridised product in an oxidising gas containing free oxygen to decompose any iron chlorides formed and finally leaching it with water to remove substantially all the remaining nickel and cobalt.

2. A process according to claim 1 in which the treatment with carbon monoxide is carried out at atmospheric pressure and at a temperature between 38 and 93°C.

3. A process according to claim 1 or claim 2 in which the treatment with chlorine gas is carried out at a temperature between 38 and 93°C and the subsequent oxidising treatment is carried out at a temperature between 93 and 260°C.

4. A process according to any of the preceding claims in which air is used as the oxidising gas.

5. A process according to any of the preceding claims in which the ore is reduced by heating at a temperature between 500 and 815°C in an atmosphere containing carbon monoxide and carbon dioxide in a ratio of not more than 3 : 2 and not less than 1 : 3 by volume so as to convert between 1% and 15% of the iron content of the ore to metal whereby the ratio of iron to nickel volatilised in the carbonyl volatilisation step is not less than 1 : 7 and not more than 2 : 1.

6. A modification of the process according to claim 5 in which the carbon monoxide and carbon dioxide in the reducing atmosphere are partly or wholly replaced by hydrogen and water vapour in an equivalent ratio.

7. A process according to claim 5 or claim 6 applied to an ore containing more than 35% iron in which the selective reduction is carried out at a temperature between 500 and 650°C.

8. A process according to claim 1 substantially as herein described with reference to any of the Examples.

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